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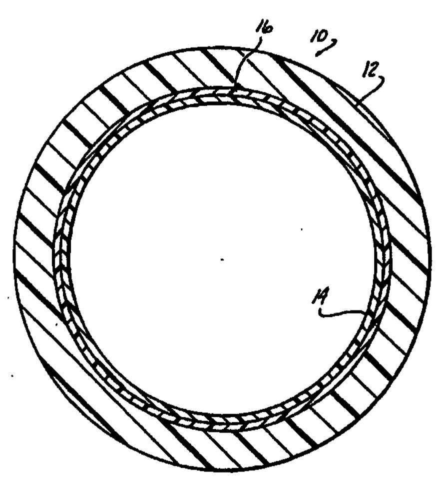

(57) Abstract

A multi-layered tubing (10) for use in a motor vehicle composed of a thick outer tubing (12) having an inner and an outer face, the outer tubing made of an extrudable thermoplastic such as a polyamide; a thin intermediate bonding layer (16) bonded to the inner face of the thick outer layer, the bonding layer composed of an extrudable melt-processible thermoplastic capable of sufficiently permanent laminar adhesion to the polyamide outer tubing; and an inner layer (14) bonded to the intermediate bonding layer, the inner layer composed of an extrudable, melt processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer. The multi-layer tubing may also include an innermost electroconductive layer and may optionally include an outer jacket.

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MULTI-LAYER FUEL AND VAPOR TUBE

I. Field of the Invention:

The present invention relates to a hose for use in a motor vehicle. More particularly, the present invention relates to a multi-layer hose which can be employed as a fuel line or vapor recovery line in a motor vehicle.

II. Background of the Invention:

Single layer fuel lines and vapor return lines of synthetic materials such as polyamides have been proposed and employed in the past. Fuel lines employing such materials generally have lengths of at least several meters. It is important that the line, once installed, not materially change during the length of operation, either by shrinkage or elongation or as a result of the stresses to which the line may be subject during use.

It is also becoming increasingly important that the lines employed be essentially impervious to hydrocarbon emissions due to permeation through the tubing. It is anticipated that future Federal and state regulations will fix the limit for permissible hydrocarbon emissions due to permeation through such lines. Regulations which will be enacted in states such as California will fix the total passive hydrocarbon emission for a vehicle at 2 g/m^2 per 24 hour period as calculated by evaporative emission testing methods such as those outlined in Title 13 of the California Code of Regulations, section 1976, proposed amendment of September 26, 1991. To achieve the desired total vehicle emission levels, a hydrocarbon permeation level for the lines equal to or below 0.5 g/m^2 per 24 hour period would be required.

Finally, it is also imperative that the fuel line employed be impervious to interaction with corrosive materials present in the fuel such as oxidative agents and surfactants as well as additives such as ethanol and methanol.

Various types of tubing have been proposed to address these concerns. In general, the most successful of these have been co-extruded multi-layer tubing which employ a relatively thick outer layer composed of a material resistant to the exterior environment. The innermost layer is thinner and is composed of a material which is chosen for its ability to block diffusion of materials such as aliphatic hydrocarbons, alcohols and other materials present in fuel blends, to the outer layer. The materials of choice for the inner layer are polyamides such as Nylon 6, Nylon 6.6, Nylon 11, and Nylon 12.

Alcohol and aromatic compounds in the fluid conveyed through the tube diffuse at different rates through the tubing wall from the aliphatic components. The resulting change in the composition of the liquid in the tubing can change the solubility thresholds of the material so as, for example, to be able to crystalize monomers and oligomers of materials such as Nylon 11 and Nylon 12 into the liquid. The presence of copper ions, which can be picked up from the fuel pump, accelerates this crystallization. The crystallized precipitate can block filters and fuel injectors and collect to limit travel of the fuel-pump or carburetor float as well as build up on critical control surfaces of the fuel pump.

In U.S. Patent Number 5,076,329 to Brunnhofer, a five- layer fuel line is proposed which is composed of a thick corrosion-resistant outer layer formed of a material known to be durable and resistant to environmental degradation such as Nylon 11 or Nylon 12. The tubing disclosed in this reference also includes a thick intermediate layer composed of conventional Nylon 6. The outer and intermediate layers are bonded together by a thin intermediate bonding layer composed of a polyethylene or a polypropylene having active side chains of maleic acid anhydride. An thin inner layer of aft rcondensed Nylon 6 with a low monomer content is

employed as the innermost region of the tubing. The use of Nylon 6 as the material in the inner fluid contacting surface is designed to eliminate at least a portion of the monomer and oligomer dissolution which would occur with Nylon 11 or Nylon 12. The thin innermost layer is bonded to the thick intermediate layer by a solvent blocking layer formed of a copolymer of ethylene and vinyl alcohol with an ethylene content between about 30% and about 45% by weight. The use of a five layer system was mandated in order to obtain a tubing with the impact resistance of Nylon 12 with the low monomer/oligomer production of Nylon 6. It was felt that these characteristics could not be obtained in a tubing of less than five layers.

In U.S. Patent Number 5,038,833 also to Brunnhofer, a three-layer fuel line without the resistance to monomer/oligomer dissolution is proposed in which a tube is formed having a co-extruded outer wall of Nylon 11 or Nylon 12, an intermediate alcohol barrier wall formed from an ethylene-vinyl alcohol copolymer, and an inner water-blocking wall formed from a polyamide such as Nylon 11 or Nylon 12. In DE 40 06 870, a fuel line is proposed in which an intermediate solvent barrier layer is formed of unmodified Nylon 6.6 either separately or in combination with blends of polyamide elastomers. The internal layer is also composed of polyamides, preferably modified or unmodified Nylon 6. The outer layer is composed of either Nylon 6 or Nylon 12.

Another tubing designed to be resistant to alcoholic media is disclosed in UK Application Number 2 204 376 A in which a tube is produced which has an thick outer layer composed of 11 or 12 block polyamides such as Nylon 11 or Nylon 12 which may be used alone or combined with 6 carbon block polyamides such as Nylon 6 or 6.6 Nylon. The outer layer may be co-extruded with an inner layer made from alcohol-resistant polyol fin co-polymer

such as a co-polymer of propylene and maleic acid. The inner layer is zinc chloride resistant Nylon 6.

Heretofore it has been extremely difficult to obtain satisfactory lamination characteristics between dissimilar polymer layers. Thus all of the multi-layer tubing proposed previously has employed polyamide-based materials in most or all of the multiple layers. While many more effective solvent-resistant chemicals exist, their use in this area is limited due to limited elongation properties, strength and compatibility with Nylon 11 and 12.

Thus it would be desirable to provide a tubing material which could be employed in motor vehicles which would be durable and prevent or reduce permeation of organic materials therethrough. It would also be desirable to provide a tubing material which would be essentially nonreactive with components of the liquid being conveyed therein.

SUMMARY OF THE INVENTION

The present invention is a multi-layer tube which can be used on motor vehicles for applications such as in a fuel line or a vapor return or recovery line. In the first and second embodiments of the present invention, the tube is composed of:

a thick flexible outer tubing having an inner and an outer face, the outer tubing consisting essentially of an extrudable melt processible thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C, the melt processible thermoplastic selected from the group consisting of six-carbon block polyamides, twelve-carbon block polyamides, eleven-carbon block polyamides, and mixtures thereof or thermoplastic elastomers commercially available under the trade names SANTOPRENE, KRATON, SARLINK, and VICHEM;

a thin intermediate bonding layer bonded to the inner face of the thick outer layer, the bonding layer

consisting essentially of an extrudable melt processible thermoplastic capable of sufficiently permanent laminar adhesion to the outer tubing; and

an inner hydrocarbon barrier layer bonded to the intermediate bonding layer, the inner layer consisting of an extrudable melt processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the thermoplastic material in the interior layer having an elongation value of at least 150% and an ability to withstand impacts of at least two ft/lbs below about -20°C.

In the third embodiment of the present invention, the tube is composed of:

a thick outer tubing having a given thickness and an inner and an outer face, the outer tubing consisting essentially of an extrudable thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C;

a thin intermediate bonding layer bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable melt-processible thermoplastic capable of sufficiently permanent laminar adhesion to the outer layer;

an interior layer bonded to the intermediate bonding layer, the interior layer consisting essentially of an extrudable, melt-processible thermoplastic material capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the thermoplastic material containing as a major constituent, a thermoplastic which is chemically dissimilar to the thermoplastic employed in the thick outer layer, the chemically dissimilar thermoplastic being resistant to perm ation and interaction with short chain aliphatic and aromatic compounds; and

an innermost electrostatic discharge integrally bonded to the multi-layer tubing, the electrostatic discharge layer consisting essentially of an extrudable, melt-processible thermoplastic material having an electrostatic dissipation capacity in a range between about 10^{-4} and about 10^{-9} ohm/cm^2.

The tubing of the present invention may also include an optional outer jacket composed of a suitable melt-processible thermoplastic which is either co-extruded or applied in a separate processing operation. The thermoplastic material employed in the optional outer jacket may be any suitable material which adds insulative or cushioning properties to the tubing jacket. The outer tubing jacket may also, optionally, be capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

DESCRIPTION OF THE DRAWING

The objects, features and advantages of the present invention will become more readily apparent from the following description, reference being made to the following drawing in which:

Fig. 1 is a sectional view through a piece of tubing of the first and second embodiments of the present invention; and

Fig. 2 is a sectional view through a piece of tubing of the third embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention is a multi-layer fuel line and vapor tube which contains at least one bonding layer and at least an outer and an inner tubing layer. The tubing of the present invention may also include at least one conductive layer. The tubing of the present invention is, preferably, fabricated by co-extruding given thermoplastic materials in a conventional co-extrusion process. The tubing may either be co-extruded to a suitable length or may be co-extruded in continuous

length and cut to fit the given application subsequently. The tubing of the present invention may have an outer diameter up to 50 mm. However, in applications such as fuel lines and vapor recovery systems, outer diameter of up to 2 to 2.5 inches are preferred.

The material may have any suitable wall thickness desired. However, in automotive systems such as those described herein, wall thicknesses between 0.5 mm and 2 mm are generally employed with wall thicknesses of approximately 0.8 to 1.5 mm being preferred. While it is within the scope of this invention to prepare a tubing material having a plurality of overlaying layers of various thermoplastic materials, the tubing of the present invention generally has a maximum of five layers inclusive of the bonding layers but excluding any outer jackets. In the first and second embodiments of the present invention, the tubing material has three or four. In the third embodiment of the present invention, the tubing material has five.

The tubing 10 of the present invention is a material which is suitable for use in motor vehicles and comprises a relatively thick outer layer 12 which is non-reactive with the external environment and can withstand various shocks, vibrational fatigue, and changes in temperature as well as exposure to various corrosive or degradative compounds to which it would be exposed through the normal course of operation of the motor vehicle.

It is anticipated that both the outer tubing layer 12 as well as any interior layers bonded thereto would be suitable for use at an outer service temperature range between about -40°C and about 150°C, with a range of -20°C to 120°C being preferred. The various layers of tubing are integrally laminated to one another and resistant to delamination throughout the lifetime of the tubing. The tubing of the present invention has a tensile strength of no l ss than $25N/mm^2$ and an

elongation value of at least 150%. The tubing has a burst strength at 23°C and 120°C of at least 20 bar. The multi-layer tubing of the present invention is sufficiently resistant to exposure to brake fluid, engine oil and peroxides such as those which may be found in gasoline.

The outer layer 12 may be composed of any melt-processible extrudable thermoplastic material which is resistant to ultra violet degradation, extreme changes in heat and exposure to environmental hazards such as zinc chloride, and degradation upon contact with engine oil and brake fluid. In general, in the first embodiment of the present invention, the outer layer 12 as depicted in Fig. 1 consists essentially of six-carbon block polyamides, such as Nylon 6, which are resistant to degradation upon exposure to zinc chloride. In the second embodiment of the present invention as depicted in Fig. 1 and third embodiment of the present invention as depicted in Fig. 2, the exterior layer is composed of a thermoplastic selected from the group consisting of twelve-carbon block polyamides, eleven-carbon block polyamides, zinc chloride resistant six-carbon block polyamides, and mixtures thereof as well as selected thermoplastic elastomers. The thermoplastic elastomers are proprietary compositions and commercially available under trade names such as SANTOPRENE, KRATON, SARLINK and VICHEM.

The materials which compose the outer layers can be employed in their respective unmodified states or can be modified with various plasticizers, flame retardants and the like in manners which would be known to one reasonably skilled in the art. In general, the respective materials which make up the outer layer 12 may be composed of any melt-processible extrudable thermoplastic material which is resistant to ultra violet degradation, extreme changes in heat and exposure to

environmental hazards such as zinc chloride, and degradation upon contact with engine oil and brake fluid.

In the first embodiment of the present invention, the exterior layer consists essentially of six-carbon block polyamides, such as Nylon 6, which either inherently exhibit sufficient resistance or contain effective amounts of suitable modifying agents to achieve such resistance to degradation upon exposure to zinc chloride.

The Nylon 6 which composes the outer layer can be employed can also be modified with various plasticizers, flame retardants and the like in manners which would be known to one reasonably skilled in the art.

In the first embodiment, the outer layer 12 is, preferably composed of a polyamide thermoplastic derived from the condensation polymerization of caprolactam. Such materials are commonly referred to as six-carbon block polyamides or Nylon 6. In this embodiment, the six-carbon block polyamide contains sufficient quantities of modifying agents to impart a level of zinc chloride resistance greater than or equal to that required by test method SAE J844; non-reactivity after 200 hour immersion in a 50% by weight aqueous zinc chloride solution. In the preferred embodiment, the six-carbon block polyamide material is a multi-component system comprised of a Nylon-6 copolymer blended with other Nylons and olefinic compound. The zinc-chloride resistant Nylon-6 of choice will have a melt temperature between about 220°C and 240°C. Examples of thermoplastic materials suitable for use in the tubing of the present invention are propriety materials which can be obtained commercially under the trade names M-7551 from NYCOA Corporation and ALLIED 1779 from Allied Chemical.

The six-carbon black polyamide may, optionally, include other modifying agents such as various plasticizing agents g nerally present in amounts between

about 1.0% and about 13% by total weight of the thermoplastic composition. as are readily known in the art. The polyamide material employed, preferably, is an impact-modified material capable of withstanding impacts of at least 2 ft. lbs. at temperatures below about -20°C.

In the second and third embodiments of the present invention, the outer layer 12 is composed of a thermoplastic selected from the group consisting of twelve-carbon block polyamides, eleven-carbon block polyamides as well as zinc chloride resistant six-carbon block polyamides, or thermoplastic elastomers. These thermoplastic elastomers are proprietary compositions and commercially available under trade names such as SANTOPRENE, KRATON, SARLINK and VICHEM. The materials which compose the outer layer in the second embodiment can be present in their unmodified state or can be modified with various plasticizers, flame retardants and the like in manners which would be known to one reasonably skilled in the art.

In the second and third embodiments, a polyamide such as Nylon 12 is, preferably, effectively employed. It is anticipated that a thermoplastic such as Nylon 12 may be either modified or unmodified. If modified, it is anticipated that the material will contain various plasticizers as are readily known in the art. In the second embodiment, the polyamide will contain up to 17% by composition weight plasticizer; with amounts between about 1% and about 13% being preferred.

In the present invention, the outer layer 12 has a wall thickness sufficient to provide suitable strength an endurance to the multi-layer tubing of the present invention. In applications involving automotive vehicles, the outer layer 12 comprises between about 50% and about 60% of the total wall thickness. In general, in the first embodiment, the outer layer has a wall thickness b tw en about 0.5 mm and about 0.8 mm; with a

preferred wall thickness between about 0.6 mm and about 0.7 mm.

In the second embodiment, the outer layer 12, preferably, has a wall thickness between about 0.5 mm and about 1 mm with a preferred range being between about 0.6 mm and about 0.8 mm. In the third embodiment, the Nylon 12 outer layer 12 preferably has a wall thickness between about 0.5 mm and about 0.8 mm; with a preferred range between about 0.6 and about 0.75 mm. As indicated previously, the tubing material of the present invention can be extruded by conventional co-extrusion methods to any continuous length desired.

The intermediate bonding layer 14 is integrally bonded to the inner surface of the thick outer polyamide layer 12. In the first and second embodiments of the present invention, the intermediate bonding layer 14 is a chemically dissimilar permeation resistant, chemical resistant, fuel resistant thermoplastic material which is melt processible in normal ranges of extrusion, i.e. about 175° to about 250°C. By the term "chemically dissimilar" it is meant that the intermediate bonding layer 14 consists essentially of a non-polyamide material which is capable of adhesion to a bonding layer interposed between the thick outer layer and the inner layer in a manner which will be described subsequently.

The material employed in the intermediate bonding layer is a thermoplastic material which permits the establishment of a homogeneous bond between the inner and outer layers and exhibits properties of resistance to permeation of aliphatic and aromatic materials such as those found in fuel. The thermoplastic material employed herein is preferably a melt-processible co-extrudable thermoplastic which may or may not contain various plasticizers and other modifying agents. In general, the material employed in the intermediate bonding layer is a mor elastic material than that employed in the associated inner layer.

In the first embodiment, the thermoplastic material which comprises the intermediate bonding layer 14 is a thermoplastic material selected from the group consisting of co-polymers of substituted or unsubstituted alkenes having less than four carbon atoms and vinyl alcohol, alkenes having less than four carbon atoms and vinyl acetate, and mixtures thereof. In this embodiment, the thermoplastic material employed will be resistant to permeation by and interaction with short chain aromatic and aliphatic compounds such as those which would be found in gasoline.

The preferred material employed in the first embodiment is a copolymer of ethylene and vinyl alcohol which has an ethylene content between about 27% and about 35% by weight with an ethylene content between about 27% and about 32% being preferred. Examples of suitable materials which can be employed in the tubing of the present invention include ethylene vinyl alcohol commercially available from EVA/LA.

In the first embodiment, the thermoplastic material employed in the intermediate bonding layer 14 is capable of serving as a hydrocarbon barrier to prevent significant permeation of the aromatic and aliphatic components of gasoline through to the polyamide outer layer of the tubing and thus, out to the surrounding environment. The effectiveness of the barrier layer at preventing such permeation will vary depending on numerous factors including but not limited to the thickness and composition of the inner layer, the thickness of the bonding layer and the composition of the materials conveyed through the tubing. It is anticipated that the bonding layer will be capable of providing the tubing of the present invention with a passive hydrocarbon permeation level less than about 0.5 g/m^2 per 24 hour.

In the second embodiment, the th rmoplastic material which comprises the interior bonding layer 16 is

a thermoplastic polyester derived from ethylen glycol selected from the group consisting of polybutylene terepthalate, polyethylene terepthalate, polyteremethylene terepthalate, and mixtures thereof. The preferred material is polybutylene terepthalate. Suitable material is commercially available under the trade name 1607 ZE40 from Hüls of Dusseldorf, Germany.

In the second embodiment, the thermoplastic material employed in the intermediate bonding layer 16 also exhibits characteristics which permit resistance to permeation by short chain aromatic and aliphatic compounds. These permeation resistant characteristics synergistically interact with the inner polyamide layer such that the total permeation resistance is unexpectedly increased when the thermoplastic interior layer is bonded to the inner polyamide layer. Thus, the resistance to permeation to short chain aromatic and aliphatic hydrocarbons exhibited by the multi-layer material exceeds the permeation resistance exhibited by individual layers of either polybutylene terepthalate or polyamide of a thickness equal to or greater than the multi-ply composite of the present invention.

In the first and second embodiments, the material employed in the intermediate bonding layer 14 can, optionally, exhibit conductive characteristics rendering it is capable of dissipation of electrostatic charges in the range of 10^{-4} to 10^{-9} ohm/cm^2. The thermoplastic material employed in the present invention may include, in its composition, a conductive media in sufficient quantity to permit electrostatic dissipation in the range defined. The conductive media may be any suitable material of a composition and shape capable of effecting this static dissipation. The conductive material may be selected from the group consisting of elem ntal carbon, stainless steel and highly conductive m tals such as copper, silver, gold, nick l, silicon and mixtures thereof. The term "el mental carbon" as used

herein is employed to describe and include materials commonly referred to as "carbon black". The carbon black can be present in the form of carbon fibers, powders, spheres, and the like.

The amount of conductive material contained in the thermoplastic is generally limited by considerations of low temperature durability and resistance to the degradative effects of the gasoline or fuel passing through the tubing. The amount of conductive material employed may be that amount sufficient to impart electrostatic dissipation characteristics to the tubing. When employed, the maximum amount of conductive material in the thermoplastic material is less than 5% by volume.

The conductive material can either be interstitially integrated into the crystalline structure of the polymer or can be co-polymerized therewith. Without being bound to any theory, it is believed that carbon-containing materials such as carbon black may be subject to carbon co-polymerization with the surrounding thermoplastic material. Materials such as stainless steel are more likely to be interstitially integrated into the crystalline structure of the polymer.

The intermediate bonding layer 14 serves to bond the thick outer layer 12 to the inner layer 16 to form a secure laminar bond therebetween. The inner layer 16 provides a stable fuel-contacting surface on the interior of the tube 10.

In the third embodiment, the tubing 10 of the present invention also includes an intermediate bonding layer 14 adhering and attached to the inner surface of the thick outer layer 12. The intermediate bonding layer 14 may be co-extruded with the other layers and is composed of a material which is capable of achieving a suitable homogeneous bond between itself, the thick outer layer and any inner layers interposed thereon. The int rmediate bonding layer 14 is generally composed of a

more elastic material than that employed in inner layers, the compositions of which will be described subsequently.

In the third embodiment, the intermediate bonding layer 14 is composed of a thermoplastic material which may exhibit properties of resistance to the permeation of aliphatic and aromatic materials such as those found in fuel in addition to exhibiting suitable bonding characteristics. The thermoplastic material employed herein is preferably a melt-processible co-extrudable fluoroplastic blend which may optionally contain various plasticizers and other modifying agents. The intermediate bonding layer 14 is, preferably, a blend containing polyvinylidine difluoride polymers, polyvinyl fluoride polymers, or mixtures thereof which exhibit an infinity to conventional polymers such as Nylon 12. In the preferred embodiment, polyvinylidine difluoride is employed. One such polymeric material suitable for use in the multi-layer tubing of the present invention is commercially available from Central Glass of Ube City, Japan under the trade designation CEFRAL SOFT XUA-2. This proprietary material is a graft copolymer of a fluorine-containing elastomeric polymer with a fluorine-containing crystalline polymer. The elastomeric polymer is, preferably, a material copolymerized from an alkyl difluoride selected from the group consisting of vinyl difluoride, vinylidine difluoride, and mixtures thereof, and a chlorofluoroalkene selected from the group consisting of ethylene chlorotrifluoroethylene. The crystalline polymer is preferably a haloalkene such as ethylene chlorotrifluoroethylene.

In the third embodiment, the bonding layer 14 is the product of the copolymerization of ethylene chlorotrifluoroethylene and a vinylidine difluoride chlorotrifluoroethylene copolymer having a melting point between about 180°C and about 210°C and a molding temperature between about 230°C and about 260°C.

The inner layer 16 may be composed of any melt-processible extrudable thermoplastic material which is resistant to ultra violet degradation, extreme changes in heat and exposure to gasoline and its additives. The material of choice may also exhibit resistance to environmental hazards such as exposure to zinc chloride, and resistance to degradation upon contact with materials such as engine oil and brake fluid.

In the first embodiment, the preferred material is a polyamide derived from the condensation polymerization of caprolactam. Suitable materials are commonly referred to as six-carbon block polyamides or Nylon 6. The six-carbon block polyamides employed herein may contain various plasticizers, fire retardants and the like as well as sufficient quantities of modifying agents to impart a level of zinc chloride resistance greater than or equal to that required by test method SAE J844: i.e. non-reactivity after 200 hour immersion in a 50% by weight aqueous zinc chloride solution.

In the first embodiment, the six-carbon block polyamide material employed is a multi-component system comprised of a Nylon-6 copolymer blended with other Nylons and olefinic compounds. The six-carbon block polyamide material of choice will is preferably resistant to zinc chloride and has a melt temperature between about 220°C and 240°C. Examples of thermoplastic materials suitable for use in the tubing of the present invention are propriety materials which can be obtained commercially under the trade names M-7551 from NYCOA Corporation and ALLIED 1779 from Allied Chemical.

In instances where the six-carbon block polyamide material employed in the first embodiment of the present invention includes plasticizing agents, these materials are generally present in amounts between about 1.0% and about 13% by total weight of the thermoplastic composition. The polyamide material employed, pr ferably, is an impact-modified material capable of

withstanding impacts of at least 2 ft. lbs. at temperatures below about -20°C.

In the first embodiment, the inner layer 16 may also contain suitable material in sufficient quantities to impart electrostatic conductivity characteristics to the tubing of the present invention. When employed, the material is preferably capable of dissipation of electrostatic charges in the range of 10^{-4} to 10^{-9} ohm/cm^2. The thermoplastic material employed in the present invention may include, in its composition, a conductive media in sufficient quantity to permit electrostatic dissipation in the range defined. The conductive media may be any suitable material of a composition and shape capable of effecting this static dissipation. The conductive material may be selected from the group consisting of elemental carbon, stainless steel and highly conductive metals such as copper, silver, gold, nickel, silicon and mixtures thereof. The term "elemental carbon" as used herein is employed to describe and include materials commonly referred to as "carbon black". The carbon black can be present in the form of carbon fibers, powders, spheres, and the like.

The amount of conductive material contained in the thermoplastic is generally limited by considerations of low temperature durability and resistance to the degradative effects of the gasoline or fuel passing through the tubing. The amount of conductive material employed may be that amount sufficient to impart electrostatic dissipation characteristics to the tubing. When employed, the maximum amount of conductive material in the thermoplastic material is less than 5% by volume.

The conductive material can either be interstitially integrated into the crystalline structure of the polymer or can be co-polymerized therewith. Without being bound to any theory, it is believed that carbon-containing materials such as carbon black may b subject to carbon co-polymerization with the surrounding

thermoplastic material. Materials such as stainless steel are more likely to be interstitially integrated into the crystalline structure of the polymer.

In the second embodiment, the thermoplastic material employed in the inner layer 14 is a melt-processible extrudable thermoplastic material resistant to extreme changes in heat and exposure to chemical intervals such as are found in engine oil and brake fluid. The thermoplastic material of choice is, preferably, chemically similar in structure and composition to the thermoplastic material employed in the thick outer layer. As used herein, the term "chemically similar material" is defined as a thermoplastic material selected from the group consisting of 12 carbon block polyamides, 11 carbon block polyamides as well as zinc chloride resistant 6 carbon block polyamides, thermoplastic elastomers and mixtures thereof. The thermoplastic elastomers which can successfully be employed in the tubing of the present invention are proprietary compositions commercially available under trade names such as SANTOPRENE, KRATON, SARLINK and VICHEM. The thermoplastic material employed in the inner layer of the tubing of the present invention either may be identical to the material employed in the thick outer layer or may be a different thermoplastic selected from those listed to take advantage of specific properties of the various thermoplastics. In the preferred embodiment, the inner layer 14 is composed of a material similar to or identical to the thick outer layer. In the preferred embodiment, a polyamide such as Nylon 12 can be effectively employed.

In the second embodiment, the thermoplastic employed in the inner layer 14 may be either modified or unmodified. If modified, it is anticipated that the material will contain various plasticizers as are readily known in th art. In the preferred embodiment, the polyamide will contain up to 17% by composition w ight

plasticizer; with amounts between about 1% and about 13% being preferred.

In the first embodiment, the inner layer has the minimum wall thickness sufficient to achieve the permeation resistance desired. In general, the inner layer is thinner than the outer layer with the thickness of the outer layer being between about 50% and about 60% of the total wall thickness of the tubing or between 55% and 60% of the thickness of the thick outer layer. In the specified embodiment, the inner wall thickness is between about 0.01 mm and about 0.2 mm with a thickness of about 0.05 mm to about 0.17 mm being preferred. The intermediate bonding layer generally may have a thickness less than or equal to that of the inner layer.

In the second embodiment, the inner layer 14 may have a thickness sufficient to supply strength and chemical resistance properties to the multi-layer tubing. Specifically, the inner layer 14 is of sufficient thickness to impede permeation of aliphatic and aromatic hydrocarbon molecules and migration of those molecules through to the thick outer layer. In the present invention, the inner layer has a wall thickness less than that of the thick outer layer. In the preferred embodiment, the inner layer has a wall thickness between about 10% and 25% that of the outer layer; preferably less than between about 0.05 mm and about 0.4 mm; with a wall thickness between about 0.1 mm and about 0.3 mm being preferred.

In the first embodiment, the intermediate bonding layer is of sufficient thickness to permit an essentially homogeneous bond between the inner and outer layers. In general, the intermediate bonding layer can be thinner than the other two layers and can constitute between about 10% and about 50% of the total wall thickness or b tw en about 20% and about 30% of the thickness of the outer layer. In the specified embodiment, the thickness of the intermediate bonding

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materials together with a fluorine-containing polymer such as copolymers of vinylidine fluoride and chlorotrifluoroethane. Suitable material employed would contain between about 60% and about 80% by weight polyvinylidine difluoride. Materials so formed have a melting point between about 200 and about 220°C and a molding temperature between about 210 and about 230°C.

In the third embodiment, the multi-layer tubing of the present invention also includes an innermost electrostatic dissipation layer 18 which is also capable of serving as a hydrocarbon barrier to assist in the prevention of permeation of aromatic and aliphatic compounds found in gasoline through to the outer layer 12 of the tubing and, thus, out to the surrounding environment.

In this third embodiment, the innermost layer 18 is integrally bonded to the inner surface of the interior layer 16. In the present invention, the interior layer 18 is composed of a thermoplastic material which is chemically dissimilar to the thermoplastic material employed in the outer layer 12 which is melt-processible in the normal ranges of extrusion, i.e. about 175°C to about 250°C. The thermoplastic material employed in the innermost layer 18 is capable of sufficiently permanent laminar adhesion to the interior layer 16.

In the third embodiment, the thermoplastic material which comprises the innermost layer 18 is selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, and mixtures thereof. The preferred material is a polyvinylidine fluoroplastic derived from the thermal dihalogenation of chlorodifluoro ethane. Suitable material is commercially available under the trade name XPV-504KRC CEFRAL SOFT CONDUCTIVE. Alternately, the innermost layer 18 may be composed of a modified material which is chemically similar to the interior layer 16.

The innermost layer 18 exhibits electrostatic conductive characteristics in that it is capable of dissipation of electrostatic charge in the range of 10^{-4} to 10^{-9} ohm/cm^2. The fluoroplastic material employed in the present invention may be inherently conductive in these ranges or, preferably, includes in its composition a conductive media in sufficient quantity to permit electrostatic dissipation in the range defined. The conductive material may be any suitable material of a composition and shape capable of effecting this static dissipation. The conductive material may be selected from the group consisting of elemental carbon, stainless steel and highly conductive metals such as copper, silver, gold, nickel, silicon and mixtures thereof. The term "elemental carbon" as used herein is employed to describe and include materials commonly referred to as "carbon black". The carbon black can be present in the form of carbon fibers, powders, spheres, and the like.

The amount of conductive material contained in the fluoroplastic is generally limited by considerations of low temperature durability and resistance to the degradative effects of the gasoline or fuel passing through the tubing. In the preferred embodiment, the fluoroplastic material contains conductive material in an amount sufficient to effect electrostatic dissipation. However, the maximum amount employed therein is less than 5% by volume.

The conductive material can either be interstitially integrated into the crystalline structure of the polymer or can be co-polymerized therewith. Without being bound to any theory, it is believed that carbon-containing materials such as carbon black may be subject to carbon co-polymerization with the surrounding fluoroplastic material. Material such as stainless steel are more likely to be interstitially integrated into the crystalline structure of the polymer.

In the third embodiment, the innermost layer 18 is maintained at thicknesses suitable for achieving static dissipation and suitable laminar adhesion respectively; generally between about 10% and 20% of the thick outer layer. The thickness of the innermost layer 18 is preferably between about 0.1 mm and about 0.2 mm. The intermediate bonding layer preferably has a thickness approximately equal to the thickness of the innermost layer preferably between about 0.05 mm and about 0.15 mm.

In the third embodiment, the interior layer 16 is maintained at a thickness suitable to achieve a hydrocarbon permeation value for the tubing of the present invention no greater than about 0.5 g/m^2 in a 24 hour interval. To accomplish this, the characteristics of the interior layer 16 can be relied upon solely or in concert with the intermediate bonding layer. It is anticipated that the thickness of the inner and intermediate layers can be modified to accomplish this end. In this embodiment, the interior layer 16 has a thickness between about 10% and about 20% of the thick outer layer. The interior layer has a thickness between about 0.15 mm and about 0.25 mm with a thickness of about 0.18 mm to about 0.22 mm being preferred. The intermediate bonding layer 14 is maintained at a thickness sufficient to permit sufficient laminar adhesion between the outer and interior layers. The intermediate bonding layer generally has a thickness less than that of the inner layer 16. The thickness of this layer is, preferably, between about 0.05 and about 0.1 mm.

The total wall thickness of the tubing of the present invention is generally between about 0.5 mm and about 2.0 mm with a wall thickness between about 0.8 and about 1.25 mm being preferred.

The tubing of the present invention may also, optionally includ an out r jacket (not shown) which surrounds the outer layer. The fourth outer jacket may

be either co-extruded with the other layers during the extrusion process or may be put on in a subsequent process such as cross-extrusion. The outer jacket may be made of any material chosen for its structural or insulative characteristics and may be of any suitable wall thickness. Preferably, the outer jacket may be made of a thermoplastic material selected from the group consisting of zinc-chloride resistant Nylon 6, Nylon 11, Nylon 12, polypropylene, and thermoplastic elastomers such as SANTOPRENE, KRATON, VICHEM and SARLINK. If desired, these materials may be modified to include flame retardants, plasticizers and the like.

In the second embodiment, the outer jacket may, preferably, exhibit conductive characteristics in that it is capable of dissipation of electrostatic charge in the range of 10^{-4} to 10^{-9} ohm/cm^2. The material which composes the outer jacket may be inherently conductive in these ranges or, preferably, includes in its composition a conductive media in sufficient quantity to permit electrostatic dissipation in the range defined. The conductive media may be any suitable material of a composition and shape capable of effecting this static dissipation. The conductive material may be selected from the group consisting of elemental carbon, stainless steel and highly conductive metals such as copper, silver, gold, nickel, silicon and mixtures thereof. The term "elemental carbon" as used herein is employed to describe and include materials commonly referred to as "carbon black". The carbon black can be present in the form of carbon fibers, powders, spheres, and the like.

The amount of conductive material contained in the outer jacket is generally limited by considerations of low temperature durability and resistance to the degradative effects of the gasoline or fuel passing through the tubing. In the preferred embodiment, the thermoplastic material contains conductive material in an amount sufficient to effect electrostatic dissipation.

However, the maximum amount employed therein is preferably less than 5% by volume.

The conductive material can either be interstitially integrated into the crystalline structure of the polymer or can be co-polymerized therewith. Without being bound to any theory, it is believed that carbon-containing materials such as carbon black may be subject to carbon co-polymerization with the surrounding thermoplastic material. Material such as stainless steel are more likely to be interstitially integrated into the the 8crystalline structure of the polymer.

What is claimed is:

1. A layered tubing for use in a motor vehicle, the tubing comprising:

a thick flexible outer tubing having an inner and an outer face, the outer tubing consisting essentially of an extrudable thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C, wherein the extrudable thermoplastic of the thick outer tubing is a melt-processible thermoplastic selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink and mixtures thereof;

a thin intermediate bonding layer bonded to the inner face of the thick outer tubing, the bonding layer consisting essentially of an extrudable melt processible thermoplastic resistant to permeation by short-chain hydrocarbons, the bonding layer consisting of a thermoplastic which is chemically dissimilar to the extrudable thermoplastic employed in the outer tubing and is capable of sufficiently permanent laminar adhesion to the inner face of the thick outer tubing; and

an inner layer having a thickness less than the thickness of the outer tubing bonded to the intermediate bonding layer, the inner layer consisting of an extrudable, melt-processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C.

2. The tubing of claim 1 wherein the outer layer is composed of a thermoplastic consisting essentially of an extrudable thermoplastic six-carbon block polyamide.

3. The tubing of claim 2 wher in the inner layer functions as a hydrocarbon barrier layer and is composed of an extrudable, melt-processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the inner layer consisting essentially of an extrudable thermoplastic six-carbon block polyamide.

4. The tubing of claim 3 wherein the inner layer is capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

5. The tubing of claim 3 wherein the inner hydrocarbon layer contains quantities of a conductive material sufficient to provide electrostatic dissipation capability in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

6. The tubing of claim 5 wherein the conductive material is selected from the group consisting of elemental carbon, copper, silver, gold, nickel, silicon, and mixtures thereof.

7. The tubing of claim 6 wherein the conductive material is present in an amount less than about 5% by volume of the polymeric material.

8. The tubing of claim 2 wherein the extrudable thermoplastic polyamide of the thick outer layer is a derived by the condensation polymerization of caprolactam.

9. The tubing of claim 8 wherein the extrudable thermoplastic polyamide of the thick outer lay r consists essentially of Nylon 6 and additive materials present in sufficient quantities to impart resistance to exposure to zinc chloride.

10. The tubing of claim 8 wherein the thick outer layer is essentially non-reactive after 200 hour immersion in a 50% by weight aqueous zinc chloride solution.

11. The tubing of claim 3 wherein the thermoplastic material employed in the intermediate bonding layer exhibits at least some resistance to interaction with short-chain hydrocarbon molecules present in material conveyed through the tubing.

12. The tubing of claim 11 wherein the thermoplastic material employed in the intermediate bonding layer includes as a major constituent an extrudable, melt processible thermoplastic selected from the group consisting of co-polymers of alkenes having less than four carbon atoms and vinyl alcohol, copolymers of alkenes having less than four carbon atoms and vinyl acetate, and mixtures thereof.

13. The tubing of claim 1 further comprising an exterior jacket overlying the thick outer tubing, the exterior jacket composed of a material consisting essentially of a thermoplastic rubber selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink and mixtures thereof.

14. The tubing of claim 1 wherein the extrudable thermoplastic of the thick outer tubing is a melt-processible thermoplastic selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink and mixtures thereof.

15. The tubing of claim 14 wherein the outer tubing comprises:

an effective amount of a polyamide selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, and mixtures thereof; and

between about 1 and about 17% by volume of a thermoplastic plasticizer material.

16. The tubing of claim 15 wherein the outer layer is composed of Nylon 12.

17. The tubing of claim 16 wherein the thermoplastic material employed in the intermediate bonding layer exhibits at least some resistance to interaction with short-chain hydrocarbon molecules present in material conveyed through the tubing.

18. The tubing of claim 17 wherein the thermoplastic material employed in the intermediate bonding layer includes as a major constituent an extrudable, melt processible thermoplastic is a thermoplastic polyester selected from the group consisting of polybutylene terepthalate, polyethylene terepthalate, polyteremethylene terepthalate, and mixtures thereof.

19. The tubing of claim 18 wherein the thermoplastic material employed in the intermediate bonding layer consists essentially of polybutylene terepthalate.

20. The tubing of claim 18 wherein the extrudable melt-processible thermoplastic of the inner layer is selected from the group consisting of Nylon 11, Nylon 12, zinc chloride-resistant Nylon 6, and mixtures thereof.

21. The tubing of claim 20 wherein the inner tubing comprises:

an effective amount of a polyamide selected from the group consisting of Nylon 11, Nylon 12, Nylon 6, and mixtures thereof; and

between about 1 and about 17% by volume of a thermoplastic plasticizer material.

22. The tubing of claim 14 further comprising an exterior jacket overlying the thick outer tubing, the exterior jacket composed of a material consisting essentially of a thermoplastic rubber selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink, and mixtures thereof.

23. The tubing of claim 22 wherein said outer jacket is capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

24. The tubing of claim 22 wherein the outer jacket contains quantities of a conductive material sufficient to provide electrostatic dissipation capability in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

25. The tubing of claim 24 wherein the conductive material is selected from the group consisting of elemental carbon, copper, silver, gold, nickel, silicon, and mixtures thereof.

26. A layered tubing for use in a motor vehicle, the tubing being resistant to hydrocarbon emissions, the tubing comprising:

an outer tubing having an inner and an outer face, the outer tubing consisting essentially of an extrudable melt processible six-carbon block polyamide having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at

temperatures below about -20°C, the six-carbon block polyamide being essentially non-reactive with zinc chloride;

an intermediate bonding layer having a thickness between about 0.01 mm and about 0.2 mm bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable thermoplastic capable of sufficiently permanent laminar adhesion to the polyamide outer tubing and exhibiting at least some resistance to short-chain hydrocarbon molecules conveyed through the tubing; and

an inner layer bonded to the intermediate bonding layer having a thickness between about 0.01 mm and about 0.2 mm, the inner layer consisting essentially of an extrudable, melt processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the inner layer consisting essentially of an extrudable thermoplastic six-carbon block polyamide having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C.

27. The tubing of claim 26 wherein the reduced hydrocarbon emission rate is less than about $0.5 g/m^2$ per 24 hour interval.

28. The tubing of claim 26 further comprising an exterior jacket overlying the thick outer tubing, the exterior jacket composed of a material consisting essentially of a thermoplastic rubber selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink, polypropylene and mixtures thereof.

29. A layered tubing for use in a motor vehicle, the tubing comprising:

an outer tubing having an inner and an outer face, the outer tubing consisting essentially of an extrudable polyamide having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C, wherein the outer tubing comprises:

a) an effective amount of a polyamide selected from the group consisting of Nylon 11, Nylon 12, Nylon 6, and mixtures thereof; and

b) between about 1 and about 17% by volume of a thermoplastic plasticizer material;

an intermediate bonding layer having a thickness between about 0.05 mm and about 0.2 mm bonded to the inner face of the thick outer tubing, the bonding layer consisting essentially of an extrudable non-polyamide thermoplastic capable of sufficiently permanent laminar adhesion to the polyamide outer tubing and exhibiting at least some resistance to short-chain hydrocarbon molecules conveyed through the tubing, wherein the extrudable thermoplastic of the intermediate bonding layer is a thermoplastic polyester selected from the group consisting of polybutylene terepthalate, polyethylene terepthalate, polymethylene terepthalate, and mixtures thereof; and

an inner layer bonded to the intermediate bonding layer having a thickness between about 0.05 mm and about 0.2 mm, the inner layer consisting essentially of an extrudable, melt processible polyamide capable of sufficiently permanent laminar adhesion with the intermediate bonding layer selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, and mixtures thereof.

30. The tubing of claim 29 further comprising an xterior jacket overlying the thick outer tubing, the exterior jacket composed of a material consisting essentially of a thermoplastic rubber selected from the

group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink, polypropylene and mixtures thereof.

31. The tubing of claim 30 wherein said outer jacket is capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

32. A layered tubing for use in a motor vehicle, the tubing comprising:

a thick flexible outer tubing having a given thickness and an inner and an outer face, the outer tubing consisting essentially of an extrudable thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C;

an intermediate bonding layer bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable melt processible thermoplastic capable of sufficiently permanent laminar adhesion to the inner face of the outer tubing;

an interior layer bonded to the intermediate bonding layer, the interior layer consisting essentially of an extrudable, melt-processible thermoplastic material capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the melt-processible thermoplastic which is chemically dissimilar to the thermoplastic employed in the thick outer layer, the chemically dissimilar thermoplastic being resistant to permeation by and interaction with short-chain aliphatic and aromatic hydrocarbon compounds; and

an innermost electrostatic dissipation layer integrally bonded to the multi-layer tubing, the electrostatic dissipation layer consisting of an extrudable, melt-processible thermoplastic material capable of sufficiently permanent laminar adhesion with

the intermediate bonding layer and of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

33. The multi-layer tubing of claim 32 wherein the interior layer is a thermoplastic material consisting essentially of a fluoroplastic material selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, and mixtures thereof.

34. The multi-layer tubing of claim 33 wherein the fluoroplastic material further consists of copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinylidine fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinyl fluoride, and mixtures thereof.

35. The multi-layer tubing of claim 34 wherein the interior layer has a thickness between about 10% and about 20% of the thick outer layer.

36. The multi-layer tubing of claim 35 wherein the innermost electrostatic discharge layer consists of a thermoplastic material which is chemically dissimilar to the thick outer layer.

37. The multi-layer tubing of claim 36 wherein the innermost electrostatic discharge layer consists essentially of a thermoplastic material which consists essentially of a fluoroplastic selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, and mixtures thereof.

38. The multi-layer tubing of claim 37 wherein the fluoroplastic material further comprises copolymers

of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinylidine fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinyl fluoride, and mixtures thereof.

39. The multi-layer tubing of claim 38 wherein the innermost electrostatic barrier layer has a thickness between about 0.1% and about 0.2% of the thick outer layer.

40. The multi-layer tubing of claim 39 wherein the innermost electrostatic dissipation layer contains quantities of a conductive material sufficient to provide electrostatic dissipation capability in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

41. The tubing of claim 40 wherein the conductive material is selected from the group consisting of elemental carbon, copper, silver, gold, nickel, silicon, and mixtures thereof.

42. The tubing of claim 41 wherein the conductive material is present in an amount less than about 5% by volume of the polymeric material.

43. The multi-layer tubing of claim 42 wherein the bonding layer is a thermoplastic material consisting essentially of:

a fluoroplastic material selected from the group consisting of ethylene dichlorotrifluoroethylene, and mixtures thereof; and

a graft copolymer selected from the group consisting of copolymers of vinylidine difluoride and chlorotrifluoroethylene copolymeriz d with polyvinylidine difluoride, copolymers of vinylidine difluoride and

chlorotrifluoroethylene copolymerized with ethylene dichlorotrifluoroethylene, and mixtures thereof.

44. The tubing of claim 43 wherein the conductive material is elemental carbon and is copolymerized with the extrudable fluoroplastic material.

45. The tubing of claim 32 wherein the extrudable thermoplastic of the thick outer tubing is a polyamide selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink and mixtures thereof.

46. The tubing of claim 32 further comprising an exterior jacket overlying the thick outer tubing, the exterior jacket composed of a material consisting essentially of a thermoplastic rubber selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink and mixtures thereof.

47. A layered tubing for use in a motor vehicle, the tubing comprising:

a thick flexible outer tubing having a given thickness and an inner and an outer face, the outer tubing consisting essentially of an extrudable polyamide having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C;

an intermediate bonding layer having a thickness between about 0.05 mm and about 0.1 mm bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable thermoplastic capable of sufficiently permanent laminar adh sion to the polyamide outer tubing;

an interior layer bonded to the intermediate bonding layer, the interior layer having a thickness

between about 0.05 mm and about 0.15 mm and consisting essentially of an extrudable, melt-processible thermoplastic material capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the melt-processible thermoplastic resistant to permeation by and interaction with short-chain aliphatic and aromatic hydrocarbon compounds selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinylidine fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinyl fluoride, and mixtures thereof; and

an innermost electrostatic dissipation layer integrally bonded to the multi-layer tubing, the electrostatic discharge layer having a thickness between about 0.1 mm and about 0.2 mm and consisting essentially of an extrudable, melt-processible thermoplastic material capable of sufficiently permanent laminar adhesion with the intermediate bonding layer and of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10^{-4} to 10^{-9} ohm/cm^2, the innermost electrostatic dissipation layer selected from the group consisting of a fluoroplastic selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinylidine fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinyl fluoride, wherein the thermoplastic material of the innermost hydrocarbon barrier layer is capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

AMENDED CLAIMS

[received by the International Bureau n 9 December 1993 (09.12.93); original claims 1, 13, 15, 21, 22, 26, 28-30, 32, 45 and 47 amended; original claims 2 and 14 cancelled; remaining claims unchanged (15 pages)]

1. A layered tubing for use in a motor vehicle, the tubing comprising:

a thick flexible outer layer having an inner and an outer face, the outer layer consisting essentially of an extrudable thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C, wherein the extrudable thermoplastic of the thick outer layer is an extrudable melt-processible zinc chloride-resistant six-carbon block polyamide;

a thin intermediate bonding layer bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable melt processible thermoplastic resistant to permeation by short-chain hydrocarbons, the bonding layer consisting of a thermoplastic which is chemically dissimilar to the extrudable thermoplastic employed in the outer layer and is capable of sufficiently permanent laminar adhesion to the inner face of the thick outer layer; and

an inner layer having a thickness less than the thickness of the outer layer bonded to the intermediate bonding layer, the inner layer consisting of an extrudable, melt-processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C.

Cancel Claim 2

3. The tubing of claim 2 wherein the inner layer functions as a hydrocarbon barrier layer and is composed of an extrudable, melt-processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the inner layer consisting essentially of an extrudable thermoplastic six-carbon block polyamide.

4. The tubing of claim 3 wherein the inner layer is capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

5. The tubing of claim 3 wherein the inner hydrocarbon layer contains quantities of a conductive material sufficient to provide electrostatic dissipation capability in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

6. The tubing of claim 5 wherein the conductive material is selected from the group consisting of elemental carbon, copper, silver, gold, nickel, silicon, and mixtures thereof.

7. The tubing of claim 6 wherein the conductive material is present in an amount less than about 5% by volume of the polymeric material.

8. The tubing of claim 2 wherein the extrudable thermoplastic polyamide of the thick outer layer is a derived by the condensation polymerization of caprolactam.

9. The tubing of claim 8 wherein the extrudable thermoplastic polyamide of the thick outer layer consists essentially of Nylon 6 and additive materials present in sufficient quantities to impart resistance to exposure to zinc chloride.

10. The tubing of claim 8 wherein the thick outer layer is essentially non-reactive after 200 hour immersion in a 50% by weight aqueous zinc chloride solution.

11. The tubing of claim 3 wherein the thermoplastic material employed in the intermediate bonding layer exhibits at least some resistance to interaction with short-chain hydrocarbon molecules present in material conveyed through the tubing.

12. The tubing of claim 11 wherein the thermoplastic material employed in the intermediate bonding layer includes as a major constituent an extrudable, melt processible thermoplastic selected from the group consisting of co-polymers of alkenes having less than four carbon atoms and vinyl alcohol, copolymers of alkenes having less than four carbon atoms and vinyl acetate, and mixtures thereof.

13. A layered tubing for use in a motor vehicle, the tubing comprising:

a thick flexible outer layer having an inner and an outer face, the outer layer consisting essentially of an extrudable thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C, wherein the extrudable thermoplastic of the thick outer layer is a melt-processible thermoplastic selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink and mixtures thereof;

a thin intermediate bonding layer bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable melt processible thermoplastic resistant to permeation by short-chain hydrocarbons, the bonding layer consisting of a

thermoplastic which is chemically dissimilar to the extrudable thermoplastic employed in the outer layer and is capable of sufficiently permanent laminar adhesion to the inner face of the thick outer layer;

an inner layer having a thickness less than the thickness of the outer layer bonded to the intermediate bonding layer, the inner layer consisting of an extrudable, melt-processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C; and

an exterior jacket overlying the thick outer tubing, the exterior jacket composed of a material consisting essentially of a thermoplastic rubber selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink and mixtures thereof.

Cancel Claim 14

15. A layered tubing for use in a motor vehicle, the tubing comprising:

a thick flexible outer layer having an inner and an outer face, the outer layer consisting essentially of an extrudable thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C, wherein the thick outer layer is a melt-processible extrudable thermoplastic comprising:

(a) an effective amount of a polyamide selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, and mixtures thereof; and

(b) between about 1 and about 17% by volume of a thermoplastic plasticizer material;

a thin intermediate bonding layer bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable melt processible

thermoplastic resistant to permeation by short-chain hydrocarbons, the bonding layer consisting of a thermoplastic which is chemically dissimilar to the extrudable thermoplastic employed in the outer layer and is capable of sufficiently permanent laminar adhesion to the inner face of the thick outer layer; and

an inner layer having a thickness less than the thickness of the outer layer bonded to the intermediate bonding layer, the inner layer consisting of an extrudable, melt-processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C.

16. The tubing of claim 15 wherein the outer layer is composed of Nylon 12.

17. The tubing of claim 16 wherein the thermoplastic material employed in the intermediate bonding layer exhibits at least some resistance to interaction with short-chain hydrocarbon molecules present in material conveyed through the tubing.

18. The tubing of claim 17 wherein the thermoplastic material employed in the intermediate bonding layer includes as a major constituent an extrudable, melt processible thermoplastic is a thermoplastic polyester selected from the group consisting of polybutylene terepthalate, polyethylene terepthalate, polyteremethylene terepthalate, and mixtures thereof.

19. The tubing of claim 18 wherein the thermoplastic material employed in the intermediate bonding layer consists essentially of polybutylene terepthalate.

20. The tubing of claim 18 wherein the extrudable melt-processible thermoplastic of the inner layer is selected from the group consisting of Nylon 11, Nylon 12, zinc chloride-resistant Nylon 6, and mixtures thereof.

21. The tubing of claim 20 wherein the inner layer comprises:

an effective amount of a polyamide selected from the group consisting of Nylon 11, Nylon 12, Nylon 6, and mixtures thereof; and

between about 1 and about 17% by volume of a thermoplastic plasticizer material.

22. A layered tubing for use in a motor vehicle, the tubing comprising:

a thick flexible outer layer having an inner and an outer face, the outer layer consisting essentially of an extrudable thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C, wherein the extrudable thermoplastic of the thick outer layer is a melt-processible thermoplastic selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink and mixtures thereof;

a thin intermediate bonding layer bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable melt processible thermoplastic resistant to permeation by short-chain hydrocarbons, the bonding layer consisting of a thermoplastic which is chemically dissimilar to the extrudable thermoplastic employed in the outer layer and is capable of sufficiently permanent laminar adhesion to the inner face of the thick outer layer;

an inner layer having a thickness less than the thickness of the outer layer bonded to the intermediate bonding layer, the inner layer consisting of an extrudable, melt-processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C; and

an exterior jacket overlying the thick outer layer, the exterior jacket composed of a material

consisting essentially of a thermoplastic rubber selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink, and mixtures thereof.

23. The tubing of claim 22 wherein said outer jacket is capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

24. The tubing of claim 22 wherein the outer jacket contains quantities of a conductive material sufficient to provide electrostatic dissipation capability in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

25. The tubing of claim 24 wherein the conductive material is selected from the group consisting of elemental carbon, copper, silver, gold, nickel, silicon, and mixtures thereof.

26. A layered tubing for use in a motor vehicle, the tubing being resistant to hydrocarbon emissions, the tubing comprising:

an outer layer having an inner and an outer face, the outer layer consisting essentially of an extrudable melt processible six-carbon block polyamide having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at

temperatures below about -20°C, the six-carbon block polyamide being essentially non-reactive with zinc chloride;

an intermediate bonding layer having a thickness between about 0.01 mm and about 0.2 mm bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable thermoplastic capable of sufficiently permanent laminar adhesion to the polyamide outer layer and exhibiting at least some resistance to short-chain hydrocarbon molecules conveyed through the tubing; and

an inner layer bonded to the intermediate bonding layer having a thickness between about 0.01 mm and about 0.2 mm, the inner layer consisting essentially of an extrudable, melt processible thermoplastic capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the inner layer consisting essentially of an extrudable thermoplastic six-carbon block polyamide having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C.

27. The tubing of claim 26 wherein the reduced hydrocarbon emission rate is less than about $0.5 g/m^2$ per 24 hour interval.

28. The tubing of claim 26 further comprising an exterior jacket overlying the thick outer layer, the exterior jacket composed of a material consisting essentially of a thermoplastic rubber selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink, polypropylene and mixtures thereof.

29. A layered tubing for use in a motor vehicle, the tubing comprising:

an outer layer having an inner and an outer face, the outer layer consisting essentially of an extrudable polyamide having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C, wherein the outer tubing comprises:

a) an effective amount of a polyamide selected from the group consisting of Nylon 11, Nylon 12, Nylon 6, and mixtures thereof; and

b) between about 1 and about 17% by volume of a thermoplastic plasticizer material;

an intermediate bonding layer having a thickness between about 0.05 mm and about 0.2 mm bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable non-polyamide thermoplastic capable of sufficiently permanent laminar adhesion to the polyamide outer layer and exhibiting at least some resistance to short-chain hydrocarbon molecules conveyed through the layer, wherein the extrudable thermoplastic of the intermediate bonding layer is a thermoplastic polyester selected from the group consisting of polybutylene terepthalate, polyethylene terepthalate, polymethylene terepthalate, and mixtures thereof; and

an inner layer bonded to the intermediate bonding layer having a thickness between about 0.05 mm and about 0.2 mm, the inner layer consisting essentially of an extrudable, melt processible polyamide capable of sufficiently permanent laminar adhesion with the intermediate bonding layer selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, and mixtures thereof.

30. The tubing of claim 29 further comprising an exterior jacket overlying the thick outer layer, the exterior jacket composed of a material consisting essentially of a thermoplastic rubber selected from the

group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink, polypropylene and mixtures thereof.

31. The tubing of claim 30 wherein said outer jacket is capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

32. A layered tubing for use in a motor vehicle, the tubing comprising:

a thick flexible outer layer having a given thickness and an inner and an outer face, the outer layer consisting essentially of an extrudable thermoplastic having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C;

an intermediate bonding layer bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable melt processible thermoplastic capable of sufficiently permanent laminar adhesion to the inner face of the outer layer;

an interior layer bonded to the intermediate bonding layer, the interior layer consisting essentially of an extrudable, melt-processible thermoplastic material capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the melt-processible thermoplastic which is chemically dissimilar to the thermoplastic employed in the thick outer layer, the chemically dissimilar thermoplastic being resistant to permeation by and interaction with short-chain aliphatic and aromatic hydrocarbon compounds; and

an innermost electrostatic dissipation layer integrally bonded to the multi-layer tubing, the electrostatic dissipation layer consisting of an extrudable, melt-processible thermoplastic material capable of sufficiently permanent laminar adhesion with

the intermediate bonding layer and of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

33. The multi-layer tubing of claim 32 wherein the interior layer is a thermoplastic material consisting essentially of a fluoroplastic material selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, and mixtures thereof.

34. The multi-layer tubing of claim 33 wherein the fluoroplastic material further consists of copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinylidine fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinyl fluoride, and mixtures thereof.

35. The multi-layer tubing of claim 34 wherein the interior layer has a thickness between about 10% and about 20% of the thick outer layer.

36. The multi-layer tubing of claim 35 wherein the innermost electrostatic discharge layer consists of a thermoplastic material which is chemically dissimilar to the thick outer layer.

37. The multi-layer tubing of claim 36 wherein the innermost electrostatic discharge layer consists essentially of a thermoplastic material which consists essentially of a fluoroplastic selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, and mixtures thereof.

38. The multi-layer tubing of claim 37 wherein the fluoroplastic material further comprises copolymers

of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinylidine fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinyl fluoride, and mixtures thereof.

39. The multi-layer tubing of claim 38 wherein the innermost electrostatic barrier layer has a thickness between about 0.1% and about 0.2% of the thick outer layer.

40. The multi-layer tubing of claim 39 wherein the innermost electrostatic dissipation layer contains quantities of a conductive material sufficient to provide electrostatic dissipation capability in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

41. The tubing of claim 40 wherein the conductive material is selected from the group consisting of elemental carbon, copper, silver, gold, nickel, silicon, and mixtures thereof.

42. The tubing of claim 41 wherein the conductive material is present in an amount less than about 5% by volume of the polymeric material.

43. The multi-layer tubing of claim 42 wherein the bonding layer is a thermoplastic material consisting essentially of:

a fluoroplastic material selected from the group consisting of ethylene dichlorotrifluoroethylene, and mixtures thereof; and

a graft copolymer selected from the group consisting of copolymers of vinylidine difluoride and chlorotrifluoroethylene copolymerized with polyvinylidine difluoride, copolymers of vinylidine difluoride and

chlorotrifluoroethylene copolymerized with ethylene dichlorotrifluoroethylene, and mixtures thereof.

44. The tubing of claim 43 wherein the conductive material is elemental carbon and is copolymerized with the extrudable fluoroplastic material.

45. The tubing of claim 32 wherein the extrudable thermoplastic of the thick outer layer is a polyamide selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink and mixtures thereof.

46. The tubing of claim 32 further comprising an exterior jacket overlying the thick outer tubing, the exterior jacket composed of a material consisting essentially of a thermoplastic rubber selected from the group consisting of Nylon 11, Nylon 12, zinc chloride resistant Nylon 6, Santoprene, Kraton, Vichem, Sarlink and mixtures thereof.

47. A layered tubing for use in a motor vehicle, the tubing comprising:

a thick flexible outer layer having a given thickness and an inner and an outer face, the outer layer consisting essentially of an extrudable polyamide having an elongation value of at least 150% and an ability to withstand impacts of at least 2 ft/lbs at temperatures below about -20°C;

an intermediate bonding layer having a thickness between about 0.05 mm and about 0.1 mm bonded to the inner face of the thick outer layer, the bonding layer consisting essentially of an extrudable thermoplastic capable of sufficiently permanent laminar adhesion to the polyamide outer layer;

an interior layer bonded to the intermediate bonding layer, the interior layer having a thickness

between about 0.05 mm and about 0.15 mm and consisting essentially of an extrudable, melt-processible thermoplastic material capable of sufficiently permanent laminar adhesion with the intermediate bonding layer, the melt-processible thermoplastic resistant to permeation by and interaction with short-chain aliphatic and aromatic hydrocarbon compounds selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinylidine fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinyl fluoride, and mixtures thereof; and

an innermost electrostatic dissipation layer integrally bonded to the multi-layer tubing, the electrostatic discharge layer having a thickness between about 0.1 mm and about 0.2 mm and consisting essentially of an extrudable, melt-processible thermoplastic material capable of sufficiently permanent laminar adhesion with the intermediate bonding layer and of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10^{-4} to 10^{-9} ohm/cm^2, the innermost electrostatic dissipation layer selected from the group consisting of a fluoroplastic selected from the group consisting of polyvinylidine fluoride, polyvinyl fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinylidine fluoride, copolymers of vinylidine difluoride and chlorotrifluoroethane copolymerized with polyvinyl fluoride, wherein the thermoplastic material of the innermost hydrocarbon barrier layer is capable of dissipating electrostatic energy, the electrostatic dissipation capacity being in a range between about 10^{-4} to 10^{-9} ohm/cm^2.

STATEMENT UNDER ARTICLE 19(1)

The Amendments to Claims 1, 13, 15, 21, 22, 26, 28, 29, 30, 32, 45 and 47 submitted herewith are to more specifically set forth the features of Applicant's invention. Such amendments generally add the subject matter of certain dependent claims to said claims to specifically describe the features of Applicant's invention and/or amend claim language to clarify the claim as amended. Claims 2 and 14 have been cancelled.

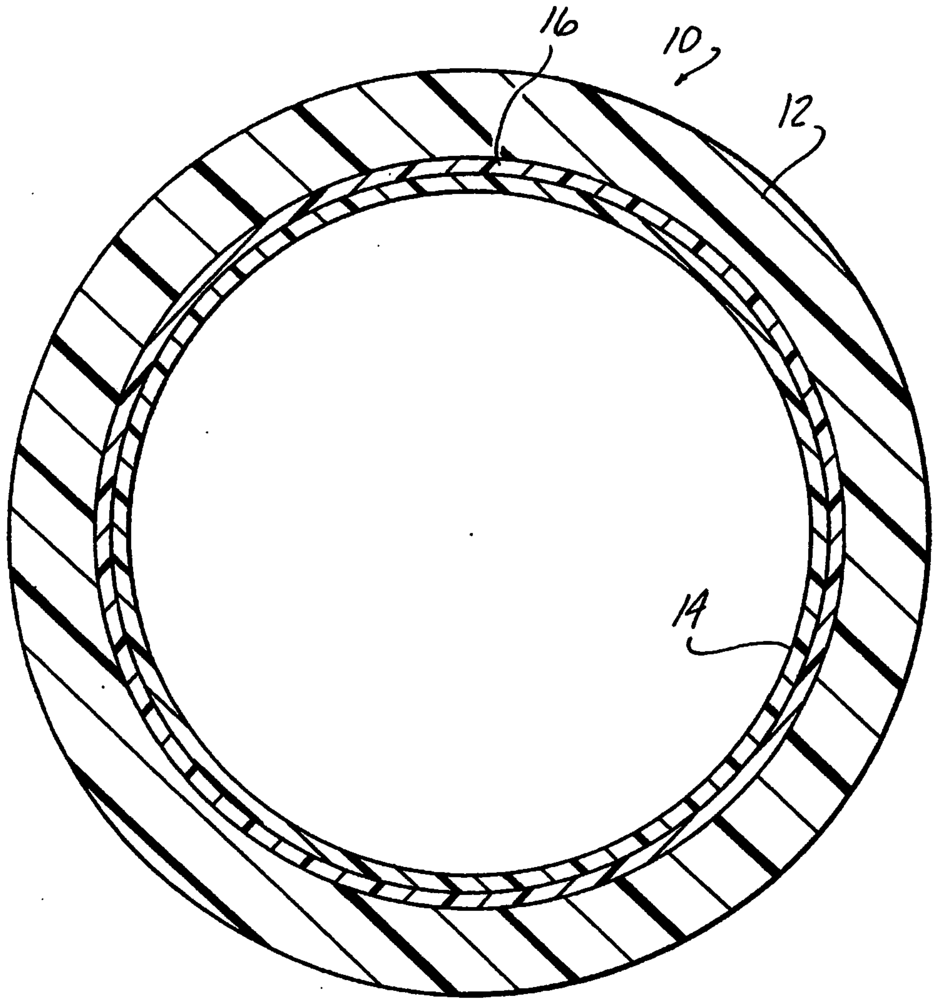

FIG-1

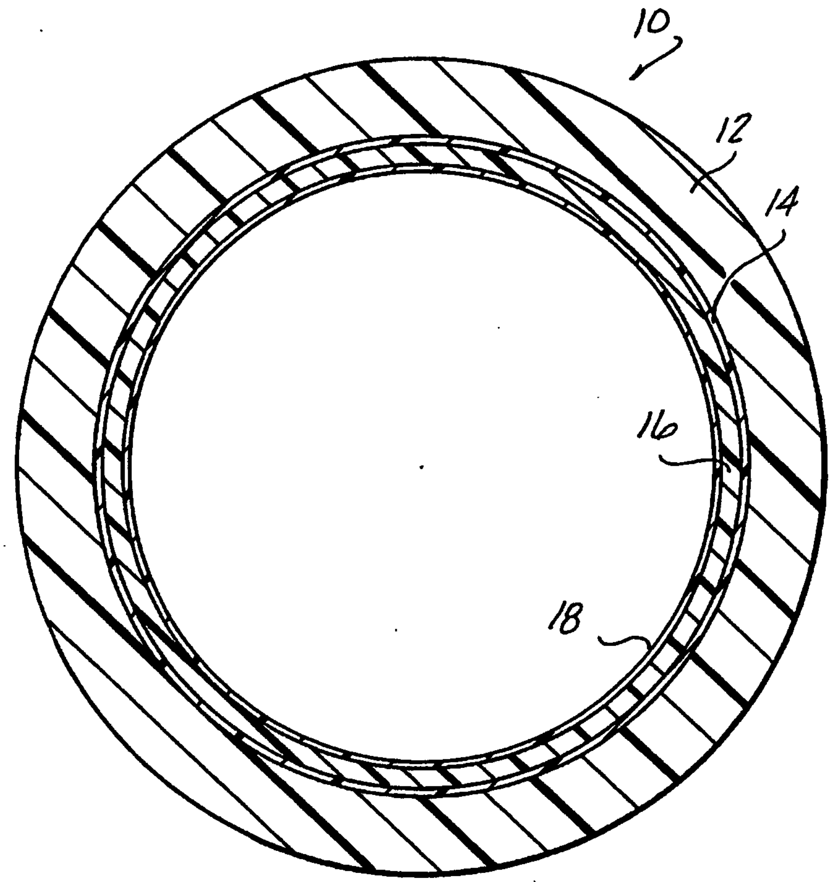

FIG-2

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/05531

I. CLASSIFICATION F SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 F16L9/12; F16L11/127

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	F16L

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	DE,C,3 827 092 (TECHNOFORM CAPRANO ET AL.) 7 September 1989 see the whole document	1
A		2,3,11, 12,14, 26,32,47
A	US,A,5 076 329 (BRUNNNHOFER) 31 December 1991 cited in the application see the whole document	1-3,26, 28,29, 32,47
A	US,A,5 038 833 (BRUNNNHOFER) 13 August 1991 cited in the application see claims 1-13	1,14-17, 26,29, 32,45,47

-/--

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

2

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
14 SEPTEMBER 1993	13. 10. 93
International Searching Authority	**Signature of Authorized Officer**
EUR PEAN PATENT FFICE	ANGIUS P.

III. DOCUMENTS CONSIDERED T BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,4 303 457 (H. A. JOHANSEN ET AL.) 1 December 1981 see abstract see column 3, line 7-12 ---	1-6,14, 22-25, 29-41,47
A	FR,A,2 114 550 (MANNESMANN AG) 30 June 1972 see claims 1-6 -----	1,2,8

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9305531
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 14/09/93
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE-C-3827092	07-09-89	None		
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		DE-U-	9007303	20-12-90
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		LU-A-	64262	02-06-72
		NL-A-	7115863	19-05-72

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82